DIELECTRIC AGING AND MICROSTRUCTURE

IN THE SYSTEM BaTiO$_3$ - CaTiO$_3$

By

F. W. Cooke
Senior Research Metallurgist
Franklin Institute, Philadelphia, Pennsylvania
Formerly at Rensselaer Polytechnic Institute

R. C. Bradt
Research Fellow at Rensselaer Polytechnic
Institute, Troy, New York

R. C. DeVries
Mineralogist at the General Electric Research
and Development Center, Schenectady, New York
and Adjunct Professor of Ceramics at
Rensselaer Polytechnic Institute

G. S. Ansell
Professor of Metallurgical Engineering
Rensselaer Polytechnic Institute
Troy, New York

TO BE SUBMITTED TO
ACTA METALLURGICA

ABSTRACT

An investigation has been made of the effect
of precipitation of a $CaTiO_3$ rich dispersed phase
on the shape, organization and thickness of ferr-
electric domains in $BaTiO_3$. No morphologically
related precipitate could be produced despite the
close structural similarity of the phases involved.
These effects have been correlated with changes in
dielectric aging behavior and it is shown that
aging is not a simple thermally activated process.

Introduction

The investigation of structure-property relationships has proven very fruitful in the analysis of metallic systems. The general purpose of this study was to use such an approach in the area of two-phase, ferroelectric ceramics. The specific purpose of this investigation was to observe the effect of a dispersed second phase on the domain structure of barium titanate and to correlate such effects with its dielectric properties, primarily with dielectric aging behavior. A secondary purpose was to study the kinetics and morphology of second phase precipitation in the system $BaTiO_3$ - $CaTiO_3$. This system was chosen because the solubility of $CaTiO_3$ in $BaTiO_3$ decreases with decreasing temperature (Figure 1). This of course is a necessary prerequisite of any system in which a second phase dispersion is to be effected by precipitation.

Dielectric aging is the decrease in the dielectric constant of barium titanate which occurs over a period of days after the material has been quenched from above its Curie temperature. Since dielectric aging is thought to be related to ferroelectric domain wall movement,[1] and since these domain

walls constitute a structural defect in the lattice, it might be expected that a dispersed second phase would have an effect on aging kinetics by interfering with wall motion. This may be thought of as dispersion hardening of dielectric behavior analogous to the dispersion hardening of mechanical properties in metallic systems.

Because of the crystallographic nature of these interactions they should be enhanced by a precipitate which is morphologically related to the matrix as is the case for a coherent precipitate or a Widmanstotten structure. $CaTiO_3$ was the ideal solute in this respect also since it has essentially the same perovskite crystal structure as $BaTiO_3$ and the lattice parameters of the terminal solid solutions differ by less than 4 per cent.[2] In addition, $CaTiO_3$ has little effect on the Curie temperature of $BaTiO_3$[3] so that this was not a complicating variable.

Experimental Procedure

Solid solution specimens were prepared from TiO_2, $BaCO_3$, and CaC_2O_4 powders which were combined in the proper proportions to produce a 20% $CaTiO_3$ alloy after reaction to form the oxides. This procedure was used to ensure stoichiometry since all commercial $BaTiO_3$ has an excess of TiO_2. To ensure homogeneity the powders were subjected to an initial blending treatment.

This consisted of calcining the powders four times at 1350°C

for 24 hours, the resulting sintered cake being ground to -240

mesh after each calcination. The blended powders were then

ground of -325 mesh and hot pressed at 1350°C for 4 hours in

graphite dies. This produced a disk specimen about 1.3 cm

in diameter and 0.3 cm thick with a density between 80 and 90%

of theoretical. The disks were solution heat treated at 1540°C

for 48 hours in air.

The lattice parameter of the $BaTiO_3$ rich phase indicated

that this treatment was sufficient to put all the $CaTiO_3$ into

solid solution and no diffraction peaks were observed other

than those due this solid solution. Electron microscopy of

high resolution, better than 100 $\overset{o}{A}$, revealed that all traces

had disappeared of the massive $CaTiO_3$ rich solid solution

particles which were present after hot pressing. In some

areas, however, a small amount, less than 0.1 volume per cent,

of fine second phase particles was present. These particles

were 0.1 micron and smaller and could not be dissolved by

solutionizing heat treatments of as long as 11 days at 1540°C

although less than 2 days was sufficient to remove all the

$CaTiO_3$ rich phase. Because of this recalcitrance, these parti-

cles have been attributed to a contaminant; probably silica

(Table I) picked up from the mortar and pestle during grinding.

The microscopic examination was performed using standard chromium shadowed carbon replicas of the polished and etched surfaces of the disks. Precipitation heat treatments were carried out at temperatures from 800°C to 1200°C, and for times from 1/2 hour to 90 hours.

BaTiO$_3$ control samples of commercial purity were prepared by both hot pressing and by cold pressing and sintering at 1400°C. The two processes produced essentially identical specimens. In addition, single crystal, solid solution specimens were prepared from the melt for microstructural comparison with polycrystalline specimens.

The aging behavior of each specimen was followed by quenching it from above the Curie point into an oil bath thermostated at the desired aging temperature. The control was better than ± 0.5°C. The aging temperatures were 100°C, 60°C and 22°C. Capacitance was measured by means of a General Radio impedance bridge, Type 1650-A at a frequency of one kilocycle and a field of one r.m.s. volt/centimeter.

Single Phase Microstructure

Figure 2 is an electron photomicrograph of pure polycrystalline barium titanate. It shows a typical system[4] of 90° and 180° domains divided by a (111) type twin. The 90° domains tend to be grouped into bands such as those observed in

large single crystals by several authors.[5-8] As is typical
of pure BaTiO$_3$, the 90° domains are quite straight and have
a mean thickness of 0.19 microns. The average grain diameter
was about 30 microns.

The single phase solid solution polycrystalline specimens
had very irregular domain structures (Figure 3) with a mean
90° domain thickness of only 0.03 microns, which is an order
of magnitude decrease from that of the pure material. No
banding was observed.

The single crystal solid solution specimens had a some-
what coarser and more regular domain structure (Figure 4)
than the polycrystalline specimens. The mean thickness of
90° domains was 0.07 microns. The most outstanding feature
of this microstructure was the pronounced banding of the 90°
domains. This supports the contention that banding is primari-
ly effected by the strain inherent in polycrystalline specimens,[6]
while the regularity and to some extent the thickness of the
90° domains depend on the amount of solute in solid solution.

Two Phase Microstructure

The most pertinent and unexpected characteristic of the
two phase microstructure was that no morphologically related
precipitate could be produced by any heat treatment. This

occurred despite the close structural similarity of the alpha and beta phases.

Precipitation heat treatments at the higher temperatures produced substantial quantities of the $CaTiO_3$ rich second phase, gamma. At 1350°C it was found that 4.6 volume per cent gamma had precipitated after one hour, and 8.6 per cent after 16 hours. At 1200°C the amount of second phase increased from 1.6 volume per cent after 1/2 hour at temperature to 7.0 volume per cent after 90 hours (Figure 5). The equilibrium amount at this temperature would be 11.5 volume per cent. At 1100°C the amounts varied from zero at 1 hour to 5.75 volume per cent after 11 hours. An activation energy for the precipitation process was determined from these data but is of little significance due to the great scatter in the data which resulted in an extremely large 95 per cent confidence interval; i.e., $E = 8.2 \pm 5.7$ K Cal/mole.

The second phase particles formed at 1200°C were generally massive, ranging in size up to 40 microns (Figure 6). In some cases the larger gamma particles completely enveloped islands of the $BaTiO_3$ solid solution (Figure 7). The 90° domain widths increased from about 0.04 microns for the shorter times to about 0.05 microns at the longer times (Table II). This coincided with a decrease in the average solute content of

the alpha phase.

At the lower temperatures, below 1000°C, the amounts of second phase never exceeded a fraction of a per cent, and the particle sizes ranged down to 0.05 microns with a mean free path between particles of about 0.5 microns (Figure 8). Thus there was no significant change in the average solute content of the alpha from that of the homogeneous solid solution, and the regularity and thickness of the 90° domains were the same as in the single phase specimens.

Capacitance

In all cases the capacitance was found to decrease with a logarithmic dependence on time after an initial transient period of several minutes (Figure 9). This is the usual behavior observed during dielectric aging.[1] Because of this logarithmic dependence, the aging rate is usually reported as the per cent decrease in capacitance per decade. In this case, all data were converted to values of the dielectric constant and the straight line portion was extrapolated back to one minute, which value was used as the initial value in computing the aging rate. For pure barium titanate, the aging rate increased from 1.7 per cent per decade at room temperature to 5.7 per cent per decade for aging at 100°C (Figure 10). It has been suggested by Mason[9] that this temperature dependence

indicates that aging is a thermally activated process. The

aging rate of the solid solution, however, was found to decrease

with aging temperature from 6.7 per cent per decade at 100°C to

1.5 per cent per decade at room temperature (Figure 10).

Thus the aging rate of pure BaTiO$_3$ increases with tempera-

ture as is characteristic of a thermally activated process,

but the aging rate of the solid solution decreases with tem-

perature which is exactly contrary to the behavior expected

of such a thermally activated process. Aging, then, must

be considered a more complex process to which the direct appli-

cation of an Arrhenius analysis is inappropriate.

The specimen with a fine dispersion of the second phase

and little change in the average solute content of the alpha

from that of the homogeneous solid solution exhibited the same

aging behavior as the solid solution. On the other hand,

specimens with significant quantities of second phase, and

hence a decreased solute content, exhibited aging behavior

which approached that of pure BaTiO$_3$. For example, as the

average composition of the BaTiO$_3$ rich solid solution de-

creased from 20 weight per cent CaTiO$_3$ to 16 weight per cent,

the 100°C aging rate increased from 1.5 per cent/decade to

4.6 per cent/decade, the aging rate of the pure BaTiO$_3$ being

5.7 per cent/decade. The aging behavior at room temperature

showed the same trend (Table III), while that at 60°C
showed no trend since the aging rate of pure BaTiO$_3$ and
the solid solution are the same at this temperature (Figure
10). Thus no effect on the aging behavior can be attributed
to the presence of a fine dispersed second phase which is
not morphologically related to the matrix. As the solute
content of the BaTiO$_3$ rich solid solution decreases, however,
the aging behavior becomes more like that of pure BaTiO$_3$.

Conclusions

From this study the following conclusions may be drawn.
The domain structure of polycrystalline BaTiO$_3$ becomes quite
irregular and the thickness of the 90° domains decreases by
an order of magnitude when as much as 20 weight per cent
CaTiO$_3$ is added in solid solution. The domain structure is
only slightly coarser and more regular in solid solution single
crystals, but the 90° domains become organized into bands
similar to those observed in pure BaTiO$_3$ single crystals.
Thus the thickness and regularity of the 90° domains is de-
pendent on alloy content as well as on the strains inherent
in polycrystalline BaTiO$_3$, while the banding behavior seems
sensitive mainly to the strains. The precipitation heat
treatments produced up to 7 volume per cent second phase at
1200°C with particle sizes up to 40 microns. Below 1000°C

only a fraction of a per cent of second phase was produced in the form of spherical particles with sizes down to less than 0.05 microns and a mean free path between particles of about 0.5 microns. The most unusual and significant result of the microstructure study was that no morphologically related precipitate could be produced by any heat treatment, despite the structural similarity of the phases involved.

The temperature dependence of the aging rate for $BaTiO_3$-$CaTiO_3$ solid solutes is just the reverse of that for unalloyed $BaTiO_3$, indicating that aging is not simply a thermally activated process. The presence of second phase particles with a dispersion comparable to the size of the $90°$ domains has no observable effect on aging behavior, but as the composition of the alpha phase approaches that of pure $BaTiO_3$, the aging behavior also becomes more like that of pure $BaTiO_3$.

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ACKNOWLEDGEMENTS

TABLE I

Analysis of $BaTiO_3$ - $CaTiO_3$ Solid Solution

after Hot Pressing

Be	0.0050 %	B	0.0030 %
Mg	0.010	Fe	0.015
Ni	0.0015	Al	0.0040
V	0.0020	Cu	0.0045
Zr	0.010	Co	0.0045

Si--Greater than 0.10%

TABLE II

Mean Thickness of 90° Domains (microns)

Precipitation Heat Treatment

Tempera-ture(°C)	1/2 Hour	1 Hour	4 Hours	10 Hours	32 Hours	90 Hours
1350	--	--	--	--	0.070 (49 Hrs.)	--
1200	0.045	0.046	0.031	0.055	0.050	0.051
1100	0.039	0.035	0.034	0.033	0.045	--

Single Phase, Solid Solution - 0.034 Microns

TABLE III

Aging Rate

Heat Treatment	Aging Rate (%/Decade)			
	Hrs.	R.T.	60°C	100°C
BaTiO₃- 20 wt.% CaTiO₃	½	7.0	5.5	2.0
	1	6.6	6.4	1.8
Hot Pressed, Solutionized	4	7.0	6.1	2.6
	10	5.9	6.5	3.6
1540°C for 2 Days, Pre-	30	6.4	3.6	3.7
	90	5.0	7.3	4.7
cipitated at 1200°C for				
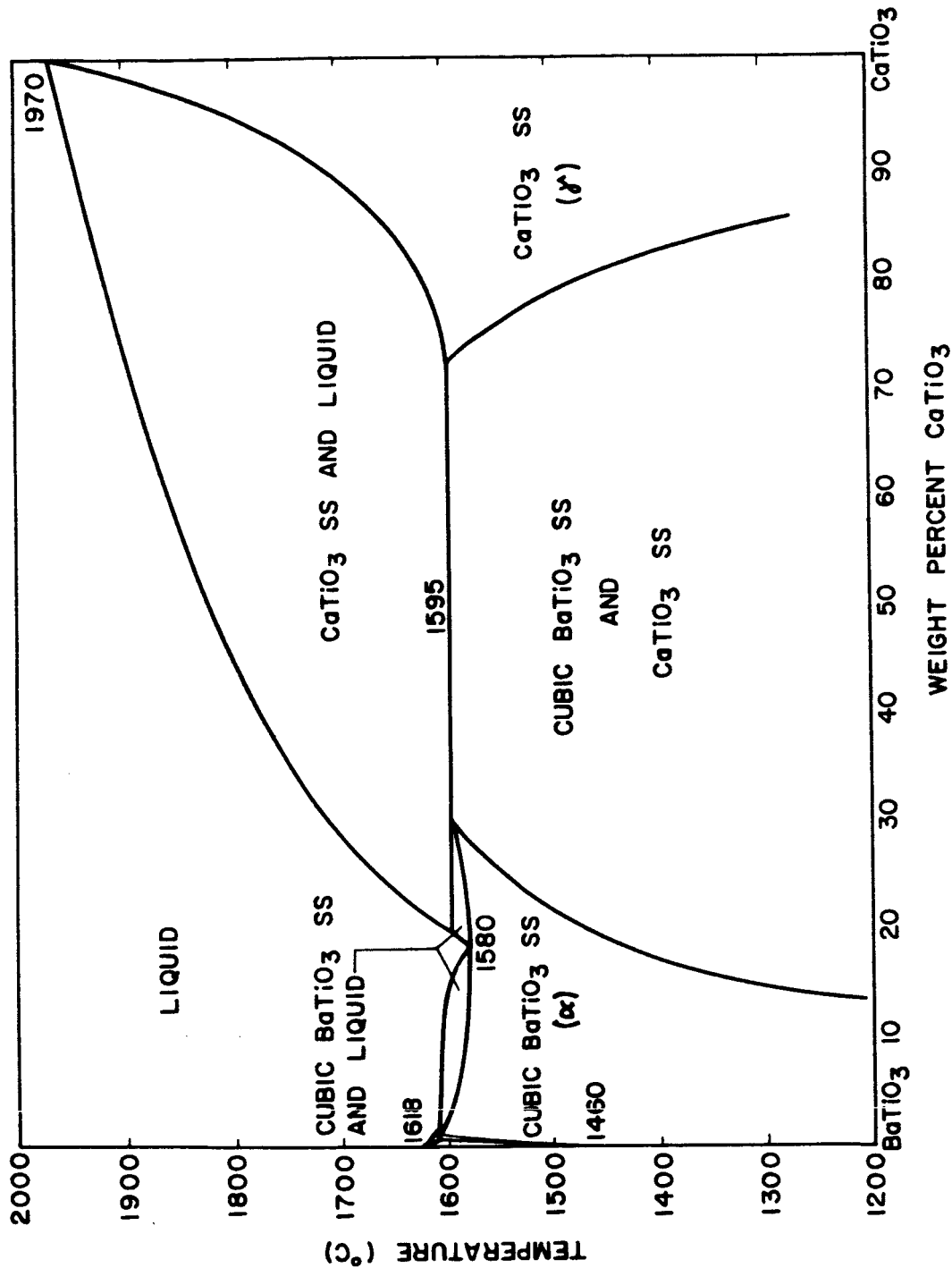
FIGURE 1. THE BARIUM TITANATE/CALCIUM TITANATE
EQUILIBRIUM DIAGRAM AFTER DEVRIES AND ROY

FIGURE 2. Pure Polycrystalline BaTiO$_3$
Straight Out. Parallel Features are 90°
Domains. (111) Twin Extends from Top Left
to Bottom. Note Banding of 90 Domains
in Upper Right. Magnification 7,300X

FIGURE 3. $BaTiO_3$ - 20 wt. % $CaTiO_3$ Polycrystalline Solid Solution. Note Fine Irregular Domain Structure. Ball at Left is 1/2 Micron Latex Sphere for Magnification and Topographical Reference. Magnification 30,000X

FIGURE 4. BaTiO$_3$ - 18 wt. % CaTiO$_3$ Single Crystal
Solid Solution. Note Banding of 90° Domains.
Magnification 7,300 X
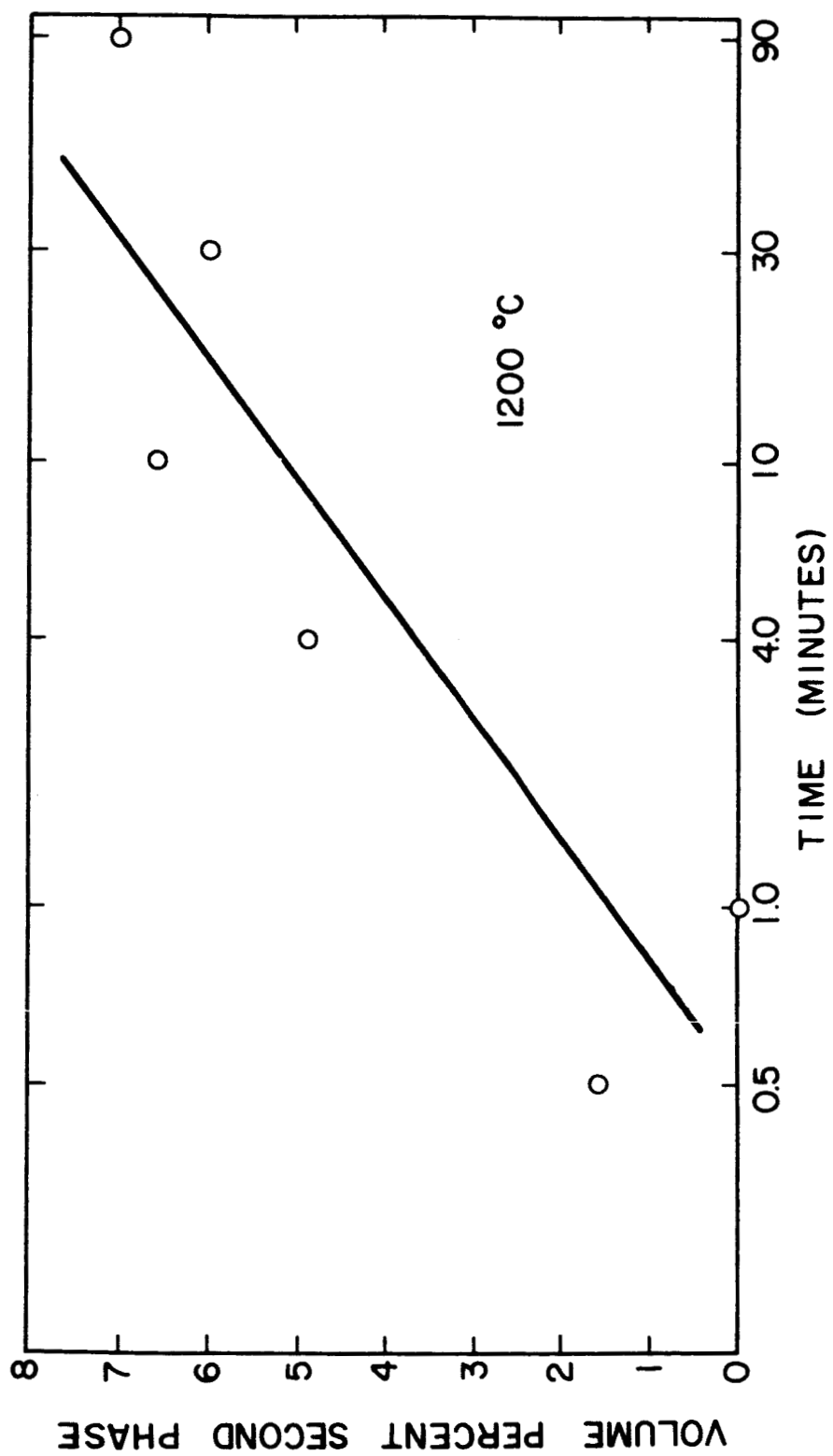
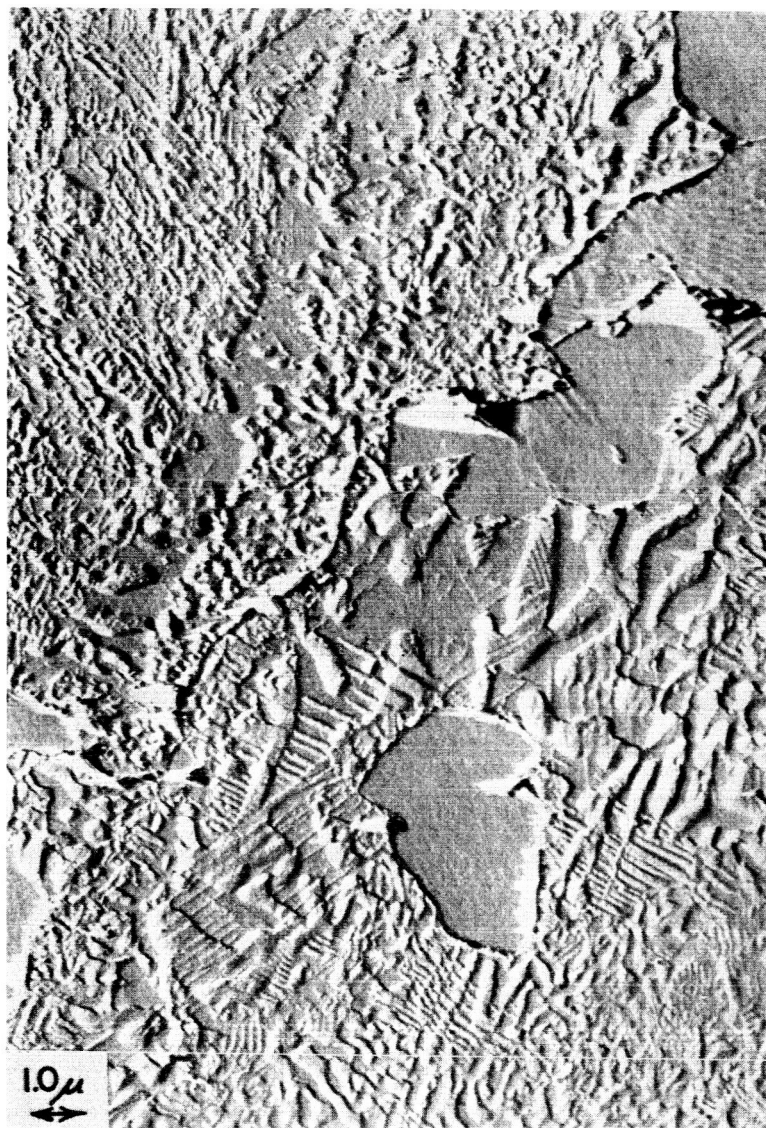FIGURE 5. VOLUME PERCENT SECOND PHASE VERSUS PRECIPITATION TIME AT 1200 °C

FIGURE 6. BaTiO$_3$ - 20 wt.% CaTiO$_3$ Precipitation
Heat Treated 90 Hours at 1200°C. Note Large
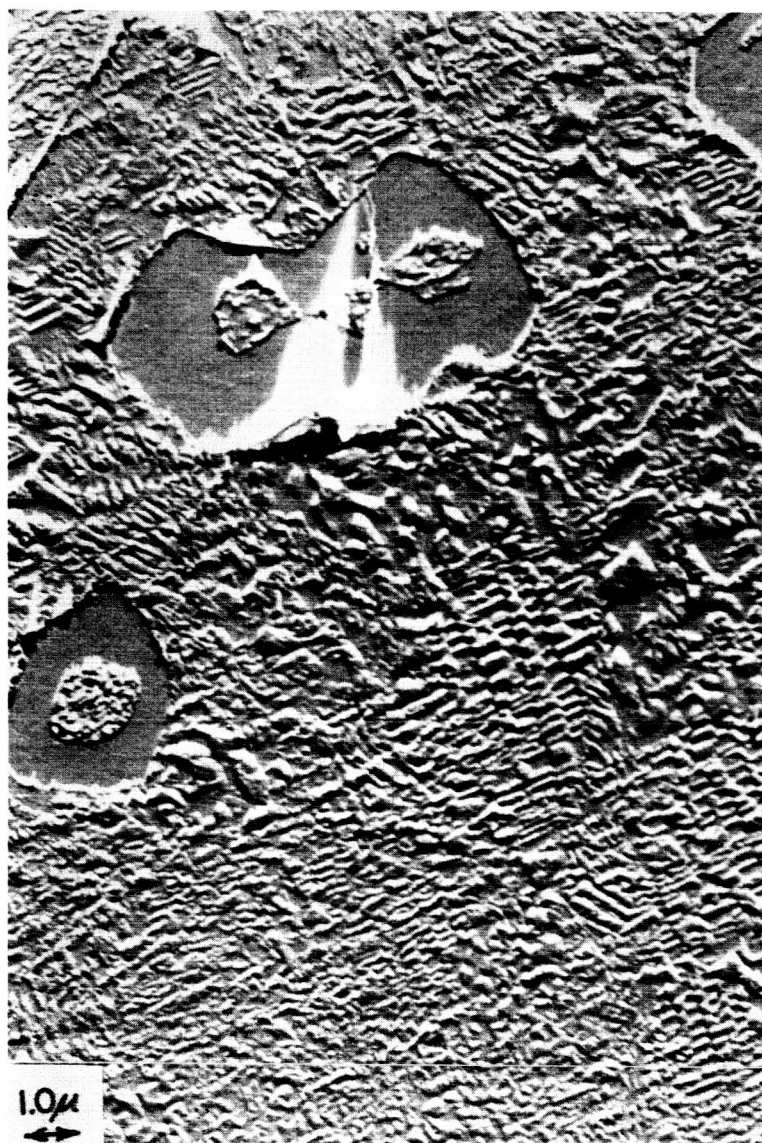Second Phase Particles with No Domain Structure
Magnification 7,300 X

FIGURE 7. $BaTiO_3$ - 20 wt.% $CaTiO_3$ Precipitation
Heat Treated at 1200°C for 90 Hours. Note
Islands of "Alpha" Surrounded by "Gamma"
Magnification 7,300 X

FIGURE 8. BaTiO$_3$ - 20 wt.% CaTiO$_3$ Precipitation
Heat Treated at 800°C for 10 Hours. Note
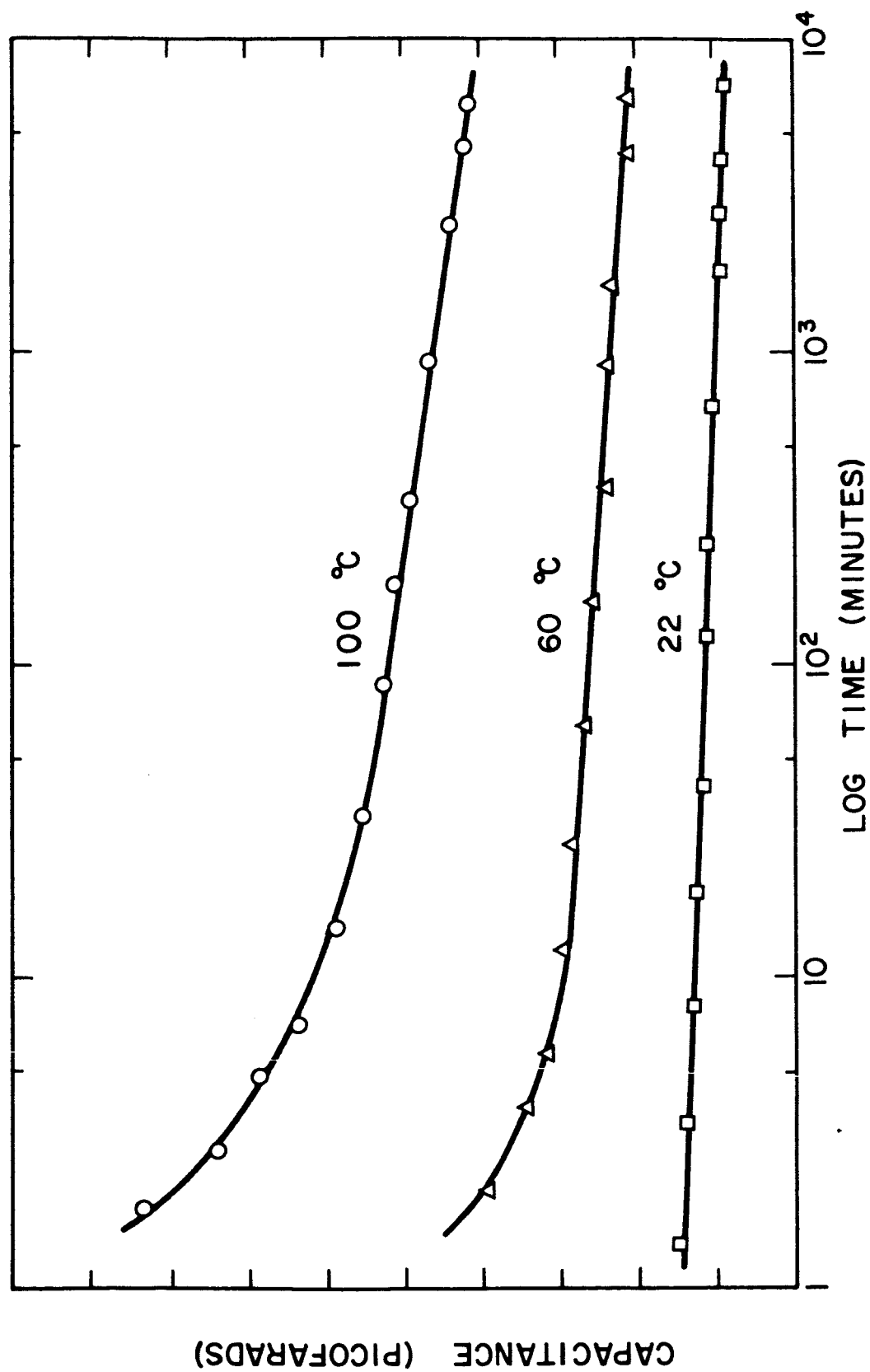Fine Particles. Magnification 8,000X

FIGURE 9. DIELECTRIC AGING OF THE SOLID SOLUTION, DEPICTED AS THE CAPACITANCE DECREASE AFTER QUENCHING FROM ABOVE THE CURIE TEMPERATURE
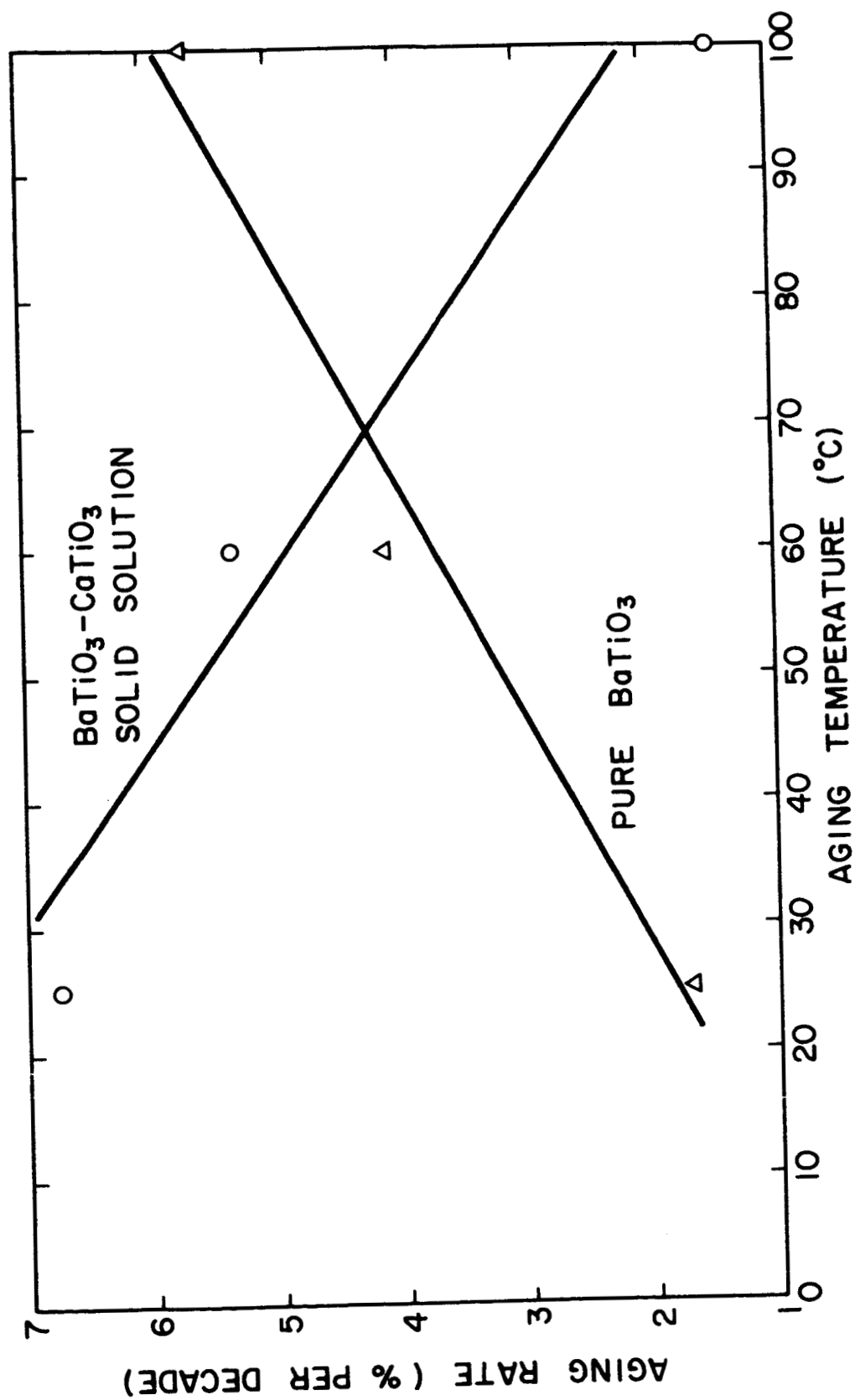
FIGURE 10. AGING RATE VERSUS AGING TEMPERATURE
FOR $BaTiO_3$ AND $BaTiO_3$-20 WT. % $CaTiO_3$ SOLID SOLUTION